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# Polariton and free-exciton-like photoluminescence in ZnO

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An unusual photoluminescence line *X* has been observed in ZnO at an energy between that of the common donor-bound excitons (DBEs) and the free excitons (FEs). In the presence of a high carrier concentration, induced by a second below-band gap laser, the DBEs decrease in intensity, due to screening, and both the FEs and *X* increase. Thus, *X* has free-exciton, rather than bound-exciton, character. However, its electric-field vector lies in the plane perpendicular to the *c* axis, as is also found for the DBEs. The appearance of *X* is discussed in terms of the polariton picture. © 2001 American Institute of Physics. [DOI: 10.1063/1.1412435]

ZnO is a semiconducting material which already is used in a variety of applications, ranging from sunscreen lotion and talcum powder to varistors,<sup>1,2</sup> piezoelectric transducers, and phosphors. Recently, however, the availability of large single crystals<sup>3</sup> has opened the way for applications, such as UV detectors, light-emitting diodes, and lasers.<sup>4</sup> In terms of band gap and optical properties, ZnO is quite similar to GaN; however, it has one big advantage over GaN and most other semiconductors, namely, a strongly bound (60 meV) free exciton. Thus, it is of paramount importance to understand the optical properties of ZnO.

Many sharp photoluminescence (PL) lines are observed at low temperatures in the near-band-edge region of high-quality, *n*-type ZnO. For example, in a sample studied earlier by our group, up to seven or eight donor-bound-exciton (*D*<sup>0</sup>*X*) lines were observed in the energy region 3.357 to 3.366 eV. Also seen are two-electron transitions of these lines at 3.314 eV (*n*=2) and 3.306 eV (*n*=3), and the free A exciton at 3.377 eV.<sup>5</sup> For that sample, of (0001) orientation, the wave vector **k** of the emitted light was travelling parallel to the crystal *c* axis, the usual case, so the electric-field **E** was always **E**⊥**c**. The polarization **E**⊥**c** favors excitons of  $\Gamma_5$  symmetry, so that those of  $\Gamma_6$  symmetry were not observed. (The lowest conduction band is of  $\Gamma_7$  symmetry and the upper valence band is of  $\Gamma_9$  symmetry;<sup>6</sup> then, excitons of symmetry  $\Gamma_5$  and  $\Gamma_6$  are possible, as determined by the cross product:  $\Gamma_7 \times \Gamma_9 = \Gamma_5 + \Gamma_6$ .) In between the bound- and free-exciton spectra, excited states (so-called “rotator” states) of the bound excitons sometimes appear in a very good crystal, such as the aforementioned one.<sup>5</sup> These will of course have the characteristics of bound excitons, not free excitons. In the present letter, we report a free-exciton-like line, appearing in this same region. We discuss its origin in terms of the polariton picture.

The ZnO sample studied here was of (10 $\bar{1}$ 0) orientation, cut from a 2 in. ingot grown by the seeded vapor transport method. Hall-effect measurements on another (10 $\bar{1}$ 0) piece

from the same ingot yielded a room-temperature mobility of 175 cm<sup>2</sup>/V s, and an electron concentration of  $1.0 \times 10^{17}$  cm<sup>-3</sup>. Unlike the previously discussed case, the (10 $\bar{1}$ 0) face contains the *c* axis, and thus the emitted light can have components with both **E**||**c** and **E**⊥**c**. Therefore, in general, we can expect unpolarized light to contain both  $\Gamma_5$  and  $\Gamma_6$  excitons. [Although, at *k*=0,  $\Gamma_6$  excitons are forbidden in both modes of polarization, still they are often seen, evidently due to the fact that the photon has finite momentum (i.e.,  $k_{\text{phot}} \neq 0$ ).]<sup>7</sup> The PL spectra were excited at 2 K with the 3250 Å line of a 45 mW HeCd laser, and additional free electrons were excited with the 5145 Å line of an Ar<sup>+</sup> ion laser. The light was dispersed with a high-resolution, 4 m, Bausch and Lomb spectrometer, and detection was accomplished with a Radio Corporation of America C31034 photomultiplier tube.

In Fig. 1, we present unpolarized spectra in the *D*<sup>0</sup>*X* region. From a polarization test, these lines are shown to have  $\Gamma_5$  character. Here, the solid line represents a spectrum obtained with excitation by the HeCd laser alone, while the dashed lines represent spectra achieved by additional irradiation

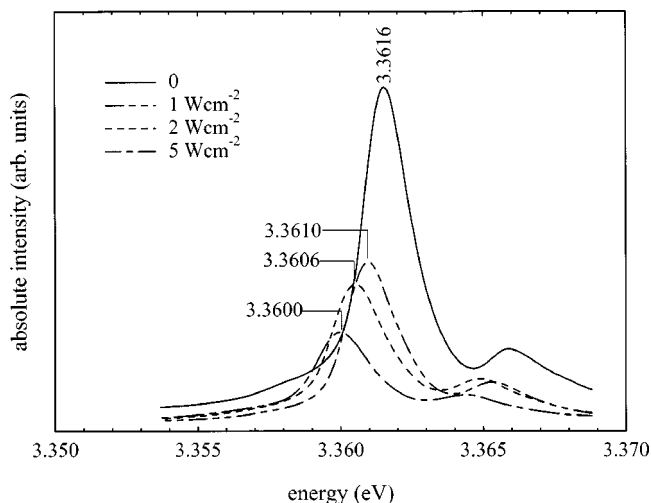


FIG. 1. Intensity of the donor-bound-exciton transitions as a function of the Ar<sup>+</sup> ion laser intensity.

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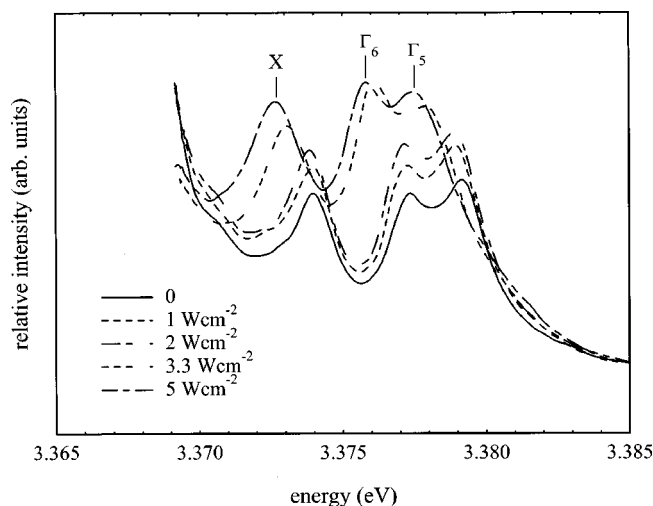


FIG. 2. Intensity of the free-exciton-like transitions as a function of the  $\text{Ar}^+$  ion laser intensity.

tion with various intensities of a second light source, an  $\text{Ar}^+$  laser. The purpose of the  $\text{Ar}^+$  laser is to excite additional free electrons, in a two-step process, and thus partially screen the bound excitons, forming free excitons. With higher  $\text{Ar}^+$ -laser intensities, the bound-exciton lines are diminished, as seen in Fig. 1. The free-exciton region is shown in Fig. 2, and it is seen that the lines increase in intensity with higher  $\text{Ar}^+$ -laser power. Also increasing in intensity is the X line, showing that it is behaving as a free exciton, not a bound exciton. Thus, X cannot be associated with a rotator state, which is an excited bound-exciton state and might be expected to appear in that same energy region. The redshift of both the free and bound excitons, with increasing  $\text{Ar}^+$ -laser intensity, occurs because of free-carrier screening and band gap renormalization, as discussed elsewhere.<sup>8</sup> The effects of a polarizer, set to favor electric-field vectors  $\mathbf{E} \parallel \mathbf{c}$ , are shown in Fig. 3. In this polarization,  $\Gamma_5$  excitons are suppressed with respect to  $\Gamma_6$  excitons. Clearly, X has  $\Gamma_5$ -like properties. In Fig. 3, another feature is observed at 3.3829 eV. This we believe is the so-called longitudinal exciton, which has mixed polarization properties.<sup>9</sup> This assignment is consistent with theory; i.e., the splitting between the transverse ( $\Gamma_5$ ) and longitudinal excitons has been given as  $\Delta E = E(\Gamma_5)4\pi\alpha/2\epsilon$ , where

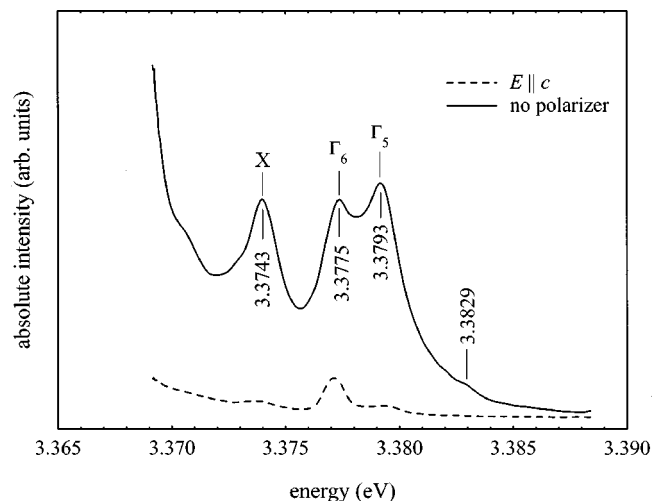


FIG. 3. Unpolarized and  $\mathbf{E} \parallel \mathbf{c}$ -polarized free-exciton-like transitions.

$E(\Gamma_5)$  is the energy of the  $\Gamma_5$  exciton,  $4\pi\alpha$  is the polarizability, and  $\epsilon$  is the dielectric constant.<sup>10</sup> From Fig. 3,  $E(\Gamma_5) = 3.379$  eV, and from the literature,<sup>9,11,12</sup>  $4\pi\alpha = 7.7 \times 10^{-3}$  and  $\epsilon = 4.0$ – $5.0$ . Thus, the predicted  $\Delta E \sim 2.6$ – $3.2$  meV, compared to our measured value of 3.6 meV. Note that Gil *et al.*<sup>10</sup> find a similar value in GaN, about 2.9 meV.

We believe that to understand the origin of X, we must invoke the polariton picture. It is well known that in strongly polar materials, transverse excitons will couple with photons to form polaritons.<sup>13–15</sup> In such a case, the usual transverse ( $\Gamma_5$ )-exciton dispersion ( $E_{\text{ex}} = E_{\text{ex},0} + \hbar^2 k_{\text{ex}}^2 / 2m_{\text{ex}}$ ) will mix with the dispersion of the photon ( $E_{\text{phot}} = \hbar c k_{\text{phot}}$ ) to produce two new dispersion curves, known as the upper polariton branch (UPB), and lower polariton branch (LPB). Note that LPBs and UPBs can occur for excitons formed from all three valence bands, A, B, and C; however, we believe that our data can be interpreted with  $\text{LPB}_A$  and  $\text{UPB}_A$  alone. Calculated polariton-dispersion curves for GaN are illustrated in several works,<sup>10,16,17</sup> and the optical spectra of ZnO are much like those of GaN.<sup>18</sup> In principle, polaritons can exist anywhere along the dispersion curves; however, the polariton lifetime  $\tau$  is higher at certain points.<sup>16</sup> We consider the PL lines in Fig. 3, from high energy to low. The 3.3829 eV line can be assigned to the so-called longitudinal exciton, as discussed. This exciton, which has been seen in many different systems, has an energy identical to that of the  $\text{UPB}_A$ , at  $k = 0$ . The next lower energy line, at 3.3793 eV, is of  $\Gamma_5$  character. This line we believe results from a high-lifetime region of the  $\text{LPB}_A$ , which of course is not at  $k = 0$ , but which has nearly the same energy as that of the free A exciton, at  $k = 0$ . (Compare the case for GaN in Fig. 3(a), Ref. 15.) Next, we come to the 3.3775 eV line, which represents an exciton of  $\Gamma_6$  character. Such excitons, which are not transverse, do not interact with the light to form polaritons, and thus have normal free-exciton dispersion curves. Therefore, this line can be assigned to a low- $k$  point of the  $\Gamma_6$  dispersion curve. (Note that the transition can not occur precisely at  $k = 0$ , because  $\Gamma_6$  excitons are unallowed at  $k = 0$ .) Finally, we must consider X, which occurs at 3.3743 eV. From the screening data of Fig. 2, and the polarization data of Fig. 3, we conclude that X has properties very similar to those of the  $\Gamma_5$  exciton on the  $\text{LPB}_A$ , as discussed. Thus, we believe that X also must be associated with the  $\text{LPB}_A$ , except that it must occur at a lower- $k$  value, since it has a lower energy. Most likely, X is in the “bottleneck” region, i.e., the region in which the photon and free-exciton dispersion curves cross. Interestingly, Torii *et al.*<sup>16</sup> see a line similar to X in GaN, i.e., one which occurs about midway between the bound-exciton and the lowest-energy polariton. Following arguments from a previous publication, they believe it is related to impurities. Such an assignment may be true in their case, especially if this line represents a rotator state of the bound exciton. However, in our case, the analogous line X does not have bound-exciton properties, so we must assume that it is a polariton on the  $\text{LPB}_A$ .

In summary, in high-quality ZnO, we have observed four lines at energies above that of the donor-bound excitons. The energies and assignments are as follows: 3.3829 eV, longitudinal exciton; 3.3793 eV,  $\Gamma_5$  exciton polariton in the high- $k$

(flat) region of the LPB<sub>A</sub>; 3.3775 eV,  $\Gamma_6$  exciton near  $k = 0$ ; and 3.3743 eV,  $\Gamma_5$  exciton polariton in the bottleneck region of the LPB<sub>A</sub>.

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